



(12) UK Patent Application (19) GB (11) 2 095 274 A

- (21) Application No 8205683
(22) Date of filing 26 Feb 1982
(30) Priority data
(31) 238620
(32) 26 Feb 1981
(31) 238619
(32) 26 Feb 1981
(31) 279550
(32) 1 Jul 1981
(31) 332006
(32) 18 Dec 1981
(31) 332005
(32) 18 Dec 1981
(31) 332004
(32) 18 Dec 1981
(31) 332008
(32) 18 Dec 1981
(31) 332007
(32) 18 Dec 1981
(33) United States of America (US)
(43) Application published 29 Sep 1982
(51) INT CL³
C11D 3/08
(52) Domestic classification
C5D 6A4B 6A5B 6A5D2
6A5E 6A5F 6A6 6A9
6B12A 6B12B1 6B12F1
6B12F2 6B12FX 6B12G2A
6B12N1 6B13 6B1 6B7
6B8 6C6
(56) Documents cited
None
(58) Field of search
C5D
(71) Applicant
Colgate-Palmolive
Company,
300 Park Avenue,
New York,
New York 10022,
United States of America
(72) Inventors
John Jerome Grecsek
Sue Wilson Giordano
Seymour Grey
(74) Agents
Kilburn and Strode,
30, John Street,
London,
WC1N 2DD

(54) Spray dried base beads and detergent compositions

(57) Free flowing, spray dried beads which are useful as a detergent or for the manufacture of a particulate built synthetic nonionic organic detergent composition include water softening aluminosilicate (such as a zeolite), bentonite and water soluble builder, and may also include water soluble synthetic organic detergent and a small proportion of water soluble silicate, although such silicate is preferably omitted. The beads can be made to be of a bulk density within a broad range, and the bulk density may be varied by control of the bead formula and by modification of spray drying conditions. The base beads and detergent compositions formulated

with them are of reduced aluminosilicate deposition characteristics, due to the presence of bentonite and the absence of or presence of only a low content of water soluble silicate, with the bead composition being maintained within given ranges. The moisture content of the beads will be such as to maintain at least 2% and preferably 3% or 4% or more of moisture in the bentonite so that its normal swelling power is retained, because the swelling of the bentonite is considered to be important in dispersing the beads in wash water and also, even more importantly, in helping to prevent aluminosilicate agglomeration and objectionable deposition thereof on materials washed, and in helping to break up any minor proportion of such agglomerates which might be formed.

GB 2 095 274 A

SPECIFICATION

Spray dried base beads and detergent compositions

This invention relates to free flowing, spray dried base beads which are useful for the manufacture of a particulate built synthetic nonionic organic detergent composition. It also relates to free flowing, spray dried detergent compositions. More particularly, the invention relates to such beads and compositions which contain certain proportions (within prescribed ranges) of a water softening aluminosilicate, such as a zeolite, bentonite, and water soluble builder for detergents. The product made is of reduced zeolite deposition characteristics compared to prior art products containing similar proportions of the water softening aluminosilicate. Such prior art products would normally also have contained appreciable proportions of water soluble silicate and usually would not have contained bentonite.

In recent years water softening insoluble aluminosilicates, such as hydrated zeolites, have been employed as builder constituents in laundry detergent compositions. Initially, renewed interest in the zeolites appears to have been stimulated by the necessity of producing detergent formulations which did not contain phosphates. Trisodium nitrilotriacetate and other salts of nitrilotriacetic acid (NTA), which had been suggested as potential replacements for the phosphates, especially for pentasodium tripolyphosphate, which had been used to a great extent in built laundry detergent compositions, had been suspected in some quarters of being harmful, and accordingly, for years compositions contained NTA were not marketed in the United States. There has never been any serious doubt that phosphates are safe for humans and recently disapproval by United States authorities of the use of NTA in detergents has been withdrawn. Accordingly, although certain non-phosphate detergent formulations will continue to be manufactured for employment in areas that are located adjacent to lakes and rivers, wherein the phosphate tends to provide a needed nutrient for algae growth and thereby may cause some eutrophication of such waters, detergent compositions contained phosphate and/or NTA are marketable once more.

Although the zeolites, preferably Zeolite A and especially preferably hydrated Zeolite 4A, have been used as builder salts in phosphate-free and NTA-free detergent composition, they have now also been found to be useful components of improved detergent and base bead compositions containing phosphate(s) and/or NTA. Normally about 6 to 12% of water soluble sodium silicate has been utilized in crutcher mixes from which spray dried base beads or detergent compositions were to be made. The silicate has been employed for its binding effect on the other components of the bead, which binding results in stable beads, and it has been discovered to help to produce a restructured structure inside the bead. It also

functions as an anti-corrosion additive which prevents or diminishes chemical attack on aluminium parts of washing machines and other appliances with which the detergent solution may come into contact. However, in proportions formerly employed e.g. 8 to 10% in the finished product, it has been noted that the combination of the water soluble silicate and the zeolite in the crutcher led to the production of aggregates of such materials in the spray dried beads, which aggregates deposited in an objectionable manner on washed materials, tending to adversely affect the appearances of the colours thereof. By means of the present invention, utilizing certain proportions of zeolite, bentonite and water soluble builder, with little or no water soluble silicate, spray dried beads of sufficient mechanical stability to be commercially acceptable can be made and these are of reduced zeolite deposition characteristics (or reduced zeolite-silicate aggregate deposition characteristics). Even when a small proportion of silicate is present it appears that the bentonite helps to counteract any tendency of the zeolite and silicate to react to produce a particle of larger size than that of the zeolite normally present i.e. as originally added to the mixture and thereby undesirable deposition of zeolite or zeolite-silicate particles on washed fabrics is prevented or lessened. Additionally, the compositions containing bentonite are much more readily disintegrated and distributed throughout the wash water, again apparently due to the presence of bentonite therein. Another advantage of the invention, when little or no silicate is employed, is that formulations containing carbonate and/or bicarbonate do not require the presence of anti-gelling materials to prevent excessive thickening of the crutcher mix. Such additives are not usually necessary when the principal builder of the detergent is a phosphate and when little or no carbonate and/or bicarbonate are present, but for non-phosphate compositions, which often will contain appreciable quantities of carbonate and/or bicarbonate, the omission of antigelling materials is decidedly advantageous, with respect to both processing and from an economic standpoint.

The prior art relating to detergent compositions, softening compositions and detergent softener compositions includes teachings that various detergent compositions can be made containing one or more of zeolite, bentonite, silicate, phosphate, NTA, quarternary ammonium compounds (softeners), and other components, usually with synthetic organic detergent, but although the disclosures contain extensive recitations (sometimes referred to as "laundry lists") if almost all materials which have been employed for any purpose in detergent and softener compositions, they do not include clear teachings or suggestions of the detergent compositions of the present invention, and this is especially true with respect to those compositions containing little or no soluble silicate. The disclosures do not appear to recognize the

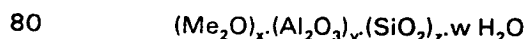
importance of the bentonite containing sufficient "lubricating" water between the plates thereof, and they do not appreciate the combination of binding and disintegrating effects attributable to the "hydrated" bentonite. Also, many of the "reference" formulas contain appreciable proportions of sodium sulphate, a filler, possible to improve the physical properties of the product particles, but such is not needed to make the compositions of the present invention which therefore can contain greater amounts of the active ingredients (including the builder).

In accordance with the present invention free-flowing, spray dried beads, useful as a detergent or for the manufacture of a particulate built synthetic nonionic organic detergent composition, which detergents are of reduced particle deposition characteristics due to the presence of bentonite and a low content of water soluble silicate or absence of such silicate in the spray dried beads, comprise by weight from 5 to 60% of water softening aluminosilicate, 2 to 40% of bentonite, containing sufficient moisture to facilitate dispersion of the bentonite so as to inhibit deposition of aluminosilicate on laundry being washed, 5 to 60% of water soluble builder or a mixture of such builders, 0 to 30% of water soluble synthetic organic detergent and 0 to 5% of water soluble silicate. The aluminosilicate may be a zeolite having a substantial exchange capacity for calcium ion, the bentonite is of appreciable swelling capacity in water and includes a sufficient proportion of moisture to facilitate disintegration of the plate-to-plate bonds thereof when the detergent beads, alone or in admixture with other detergent components, are placed in water, the water soluble builder or builder mixture is a polyphosphate, nitrilotriacetate or carbonate, and there is no water soluble silicate present. Also within the invention are detergent compositions made by spray drying the described bead formula with an anionic detergent present in the crutcher mix or by spraying nonionic detergent in liquid form onto tumbling detergent-free beads or beads containing only relatively small proportions of anionic detergent or mixtures of anionic detergents. Mixtures of such compositions, mixed anionic and nonionic detergent compositions, are also useful and may possess superior washing properties.

The zeolites employed include crystalline, amorphous and mixed crystalline-amorphous zeolites, of both natural and synthetic origins, which are of satisfactorily quick and sufficiently effective activities in counteracting calcium hardness ions in wash waters. Preferably, such materials are capable of reacting sufficiently rapidly with the calcium ions so that, alone or in conjunction with other water softening compounds in the detergent, they soften the wash water before adverse reactions of such ions with other components of the synthetic organic detergent composition occur. The zeolites employed may be characterized as having a high

exchange capacity for calcium ion, which is normally from about 200 to 400 or more milligram equivalents of calcium carbonate hardness per gram of the aluminosilicate, preferably 250 to 350 mg. e.q./g. Also they preferably have a hardness depletion rate residual hardness of 0.02 to 0.05 mg. CaCO₃/litre in one minute, preferably 0.02 to 0.03 mg./l., and less than 0.01 mg./l. in 10 minutes, all on the anhydrous zeolite basis.

Although other ion exchanging zeolites may also be utilized, normally the finely divided synthetic zeolite builder particles employed in the practice of this invention will be of the formula



wherein Me represents a metal or other suitable cationic material, x is 1, y is from 0.8 to 1.2, preferably about 1, z is from 1.5 to 3.5, preferably 2 to 3 or about 2, and w is from 0 to 9, preferably 2.5 to 6.

The zeolite should preferably be a univalent cation-exchanging zeolite, i.e., it should be an aluminosilicate of a univalent cation such as sodium, potassium, lithium (when practicable) or other alkali metal, ammonium or hydrogen (sometimes). Preferably the univalent cation of the zeolite molecular sieve is an alkali metal cation, especially sodium or potassium, and more preferably it is sodium.

Crystalline types of zeolites utilizable as good ion exchangers in the invention, at least in part, include zeolites of the following crystal structure groups: A, X, Y, L, mordenite and erionite, of which types A, X, and Y are preferred. Mixtures of such molecular sieve zeolites can also be useful, especially when type A zeolite is present. These crystalline types of zeolites are well known in the art and are more particularly described in the text *Zeolite Molecular Sieves*, by Donald W. Breck, published in 1974 by John Wiley & Sons. Typical commercially available zeolites of the aforementioned structural types are listed in Table 9.6 at pages 747—749 of the Breck text.

Such zeolites are known in the art. Some, and other such suitable zeolites have been described in many patents in recent years for use as detergent composition builders.

The zeolite used in the invention is usually synthetic and it is often characterised by a network of substantially uniformly sized pores in the range of about 3 to 10 Angstroms, often being about 4 Å (nominal), such size being uniquely determined by the unit structure of the zeolite crystal. Preferably it is of type A or similar structure, particularly described at page 133 of the aforementioned text. Good results have been obtained when a type 4A molecular sieve zeolite is employed, wherein the univalent cation of the zeolite is sodium and the pore size of the zeolite is about 4 Angstroms, and such zeolites are preferred. Such zeolite molecular sieves are described in U.S. patent 2,882,243, which refers to them as Zeolite A.

Molecular sieve zeolites of ion exchanging and water softening properties can be prepared in either a dehydrated or calcined form, which contains from about 0 or about 1.5% to about 3% of moisture, or in a hydrated or water loaded form which contains additional bound water in an amount from about 4% up to about 36% of the zeolite total weight, depending on the type of zeolite used. The water containing hydrated form of the molecular sieve zeolite (preferably hydrated to about 15 to 70% of capacity is preferred in the practice of this invention when a crystalline product is to be used. The manufacture of such crystals is well known in the art. For example, in the preparation of Zeolite A, referred to above, the hydrated zeolite crystals that are formed in the crystallization medium (such as a hydrous amorphous sodium aluminosilicate gel) are used without undergoing high temperature dehydration (calcining to 3% or less water content) that is normally practiced in preparing such crystals for use as catalysts, e.g., cracking catalysts. The crystalline zeolite, in either completely hydrated or partially hydrated form, can be recovered by filtering off the crystals from the crystallisation medium and drying them in air at ambient temperature so that their water contents are in the range of about 5 to 30%, preferably about 10 or 15 to 25%, such as 17 to 22%, e.g., 20%. However, the moisture content of the molecular sieve type zeolite being employed may be lower, as was previously described, in which case the zeolite can be hydrated during crutching and other processing.

Preferably the zeolite should be in a finely divided state, with the ultimate particle diameters being up to 20 microns, e.g., 0.005 or 0.01 to 20 microns, more preferably being from 0.01 to 15 microns, e.g., 3 to 12 microns, and especially preferably being of 0.01 to 8 microns mean particle size, e.g., 3 to 7 microns, if crystalline, and 0.01 to 0.1 micron, e.g., 0.01 to 0.05 micron, if amorphous. Although the ultimate particle sizes are much lower, usually the zeolite particles will be of sizes within the range of 100 to 400 mesh, preferably 140 to 325 mesh. These are U.S. mesh sizes; U.S. 100 mesh has openings of 149 microns, 140 mesh of 105 microns, 325 mesh of 44 microns and 400 mesh of 37 microns. Zeolites of smaller sizes will often become objectionable dusty and those of larger sizes may not sufficiently and satisfactorily attach to carbonate, bicarbonate, phosphate and/or NTA base particles nuclei on which they may be distributed with the bentonite, such as in a gel-like or film state, during spray drying of a crutcher mix to form base beads.

The bentonite employed is preferably a colloidal clay (aluminium silicate) containing montmorillonite. Montmorillonite is a hydrated aluminium silicate in which about 1/6th of the aluminium atoms may be replaced with magnesium atoms and with which varying amounts of hydrogen, sodium, potassium, calcium, magnesium and other metals may be

loosely combined. The type of bentonite clay which is most useful in making the base beads of the present invention is that which is known as sodium bentonite (or Wyoming or western bentonite), which is normally a light to cream-coloured impalpable powder which, in water, forms a colloidal suspension having strongly thixotropic properties. In water the swelling capacity of the clay will usually be in the range of 3 to 5 ml/gram, preferably 7 to 15 ml/gram, and its viscosity, at a 6% concentration in water, will usually be in the range of 3 to 30 centipoises, preferably 8 to 30 centipoises.

Preferred swelling bentonites of this type are sold under the trademark Mineral Colloid, as industrial bentonites, by Benton Clay Company, an affiliate of Georgia Kaolin Co. These materials which are the same as those formerly sold under the trademark THIXO-JEL, are selectively mined and beneficiated bentonite, and those considered to be most useful are available as Mineral Colloid No's 101, etc., corresponding to THIXO-JELS No's 1, 2, 3 and 4. Such materials have pH's (at 6% concentration in water) in the range of 8 to 9.4, maximum free moisture contents of about 8% and specific gravities of about 2.6, and for the pulverized grade about 85% passes through a 200-mesh U.S. sieve series sieve (200 mesh has openings of 74 microns). Beneficiated Wyoming bentonite is preferred as a component of the present compositions but other bentonites are also useful, especially when they form a minor proportion of the bentonite used. Although it is desirable to limit maximum free moisture content, as mentioned, it is even more important to make certain that the bentonite being employed includes enough free moisture, most of which is considered to be present between adjacent plates of the bentonite, to facilitate quick disintegration of the bentonite and any adjacent materials in the particles when such particles or detergent compositions containing them are brought into contact with water, such as wash water. It has been found that at least about 2%, preferably at least 3% and more preferably, about 4% or more of water should be present in the bentonite initially, before it is admixed with the other bead components in the crutcher, and such proportion should also be present after spray drying. In other words, overdrying to the point where the bentonite loses its "internal" moisture can significantly diminish the utility of the present compositions. When the bentonite moisture content is too low the bentonite does not act to prevent silicate-zeolite agglomerates being formed and it also does not aid in disintegrating the beads in the wash water. When the bentonite is of satisfactory moisture content it exhibits an exchangeable calcium oxide percentage in the range of about 1 to 1.8 and with respect to magnesium oxide such percentage is normally in the range of 0.04 to 0.41. Typical chemical analyses of such materials are from 64.8 to 73.0% of SiO_2 , 1.4 to 1.8% of Al_2O_3 , 1.6 to 2.7% of MgO , 1.3 to 3.1% of CaO , 2.3 to 3.4% of Fe_2O_3 ,

0.8 to 2.8% of Na_2O and 0.4 to 7.0% of K_2O .

The water soluble builder or mixture thereof employed may be one or more of the conventional materials that have been used as builders or suggested for such purpose. These include inorganic and organic builders, and mixtures thereof. Among the inorganic builders those of preference are the various phosphates, preferably polyphosphates, e.g., tripolyphosphates and pyrophosphates, such as pentasodium tri-polyphosphate and tetrasodium pyrophosphate. Trisodium nitrilotriacetate (NTA), preferably employed as the monohydrate, and other nitrilotriacetates, such as disodium nitrilotriacetate, are preferred water soluble builders. Sodium tri-polyphosphates, sodium pyrophosphate and NTA may be utilized in hydrated forms but even when anhydrous compounds are used the bentonite and zeolite appear to inhibit caking due to subsequent hydration. Carbonates, such as sodium carbonate, are useful builders and may desirably be employed, alone or in conjunction with bicarbonates, such as sodium bicarbonate. When the polyphosphates are employed it may be preferred to have sodium pyrophosphate present with sodium tripolyphosphate in proportion from 1:10 to 10:1, preferably 1:5 to 5:1 with respect to it, with the total proportion of both builders being about the same as that mentioned herein for the sodium tripolyphosphate. Other water soluble builders that are considered to be effective include the various other inorganic and organic phosphates, borates, e.g., borax, citrates, gluconates, ethylene diamine tetracetic acid (EDTA) and iminodiacetates. Preferably the various builders will be in the form of their alkali metal salts, either the sodium or potassium salts, or a mixture thereof, but sodium salts are normally more preferred. In some instances, as when neutral or slightly acidic detergent compositions are being produced, acid forms of the builders, especially of the organic builders, may be preferable but normally the salts will either be neutral or basic in nature. The silicates, preferably sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio within the range of 1:1.6 to 1:3.0, preferably 1:2 to 1:2.8 e.g., 1:2.35 or 1:2.4 also serve as builder salts but because of their strong binding properties and their characteristic of promoting aggregation or agglomeration with zeolite particles, they are special cases of builders and it is preferred that they are omitted from the present compositions. However, because they do possess anti-corrosion properties, especially important when the detergent solution is to be employed in washing machines or other appliances in contact with aluminium parts thereof, they may sometimes be present in limited small proportions. In such instances it may be preferable for hydrated sodium silicate particles to be post-added, so that they do not react with or agglomerate with zeolite particles in the crutching and spray drying operations. Although sodium sulphate and sodium chloride and other filler salts possess no building properties they are

sometimes utilized in detergent compositions for their filling characteristics. In addition to increasing the volume and weight of the product to facilitate measuring, they also sometimes improve bead stabilities and physical properties of the detergent composition beads in which they are incorporated. Nevertheless, because the present compositions are satisfactory without any fillers being present, such are preferably avoided entirely or any proportion thereof present is minimized, usually to a practical minimum.

Usually the detergent(s) employed will normally be either nonionic or anionic or both but amphoteric or ampholytic detergents may also be used, especially in conjunction with nonionics and/or anionics in the present compositions. Cationic detergents may serve as fabric softeners in these products but normally will not be spray dried with anionic detergents, due to an undesirable interaction that can take place. These classes of materials are well known and have been described repeatedly in the detergent art. Because they are not preferred components of the present compositions no further descriptions thereof in this specification is considered to be appropriate.

Although various nonionic detergents of satisfactory physical characteristics may be utilized, including condensation products of ethylene oxide and propylene oxide with each other and with hydroxyl-containing bases such as nonyl phenol and Oxo-type alcohols, it is highly preferred that the nonionic detergent be a condensation product of ethylene oxide and higher fatty alcohol. In such products the higher fatty alcohol may be of 10 to 20 carbon atoms, preferably 12 to 16 carbon atoms, and the nonionic detergent may contain from about 3 to 20 or 30 ethylene oxide groups per mol, preferably from 6 to 12. Most preferably, the nonionic detergent will be one in which the higher fatty alcohol is of about 12 to 13 or 15 carbon atoms and which contains from 6 to 7 or 11 mols of ethylene oxide. Such detergents are made by Shell Chemical Company and are available under the trade names Neodol (Registered Trade Mark) 23—6.5 and 25.7. Among their specially attractive properties, in addition to good detergency with respect to oily marks on goods to be washed, is a comparatively low melting point, yet appreciably above room temperature, so that they may be sprayed onto base beads as a liquid which solidifies.

Various anionic detergents, usually as sodium salts, may be employed but those which are most preferred are linear higher alkyl benzene sulphonates, higher alkyl sulphates and higher fatty alcohol polyethoxylate sulphates. Preferably, in the higher alkyl benzene sulphonate the higher alkyl group is linear and of 12 to 15 carbon atoms, e.g., 13, and is a sodium salt. The alkyl sulphate is preferably a higher fatty alkyl sulphate of 10 to 18 carbon atoms, preferably 12 to 16 carbon atoms, e.g., 12, and is also employed as the sodium salt. The higher alkyl ethoxamer sulphates will similarly be of 10 or 12 to 18

carbon atoms, e.g. 12, in the higher alkyl group, which will preferably be a fatty alkyl group, and the ethoxy content will normally be from 3 to 30 ethoxy groups per mol, preferably 3 or 5 to 20.

- 5 Again, the sodium salts are preferred. Thus, it will be seen that the alkyl groups are preferably linear or fatty higher alkyl groups of 10 to 18 carbon atoms, the cation is preferably sodium, and when a polyethoxy chain is present the sulphate group
- 10 is at the end thereof. Other useful anionic detergents include the higher olefin sulphonates and paraffin sulphonates, e.g., the sodium salts wherein the olefin or paraffin groups are of 10 to 18 carbon atoms. Specific examples of the
- 15 preferred detergents are sodium tridecyl benzene suphonate, sodium tallow alcohol polyethoxy (3 EtO) sulphate, and sodium hydrogenated tallow alcohol sulphate. In addition to the preferred anionic detergents mentioned, others of this well
- 20 known group may also be present, especially in only minor proportions with respect to those previously described. Also, mixtures thereof may be employed and in some cases such mixtures can be superior to single detergents. The various
- 25 anionic detergents are well known in the art and are described at length at pages 25 to 138 of the text *Surface Active Agents and Detergents*, Vol. II, By Schwartz, Perry and Berch, published in 1958 by Interscience Publishers, Inc.
- 30 Various adjuvants may be present in the crutcher mix from which base beads or detergent compositions may be spray dried, or such adjuvants may be post-added, with the decision as to the mode of addition often being determined
- 35 by the physical properties of the adjuvant, its resistance to heat, its resistance to degradation in the aqueous crutcher medium, and its volatility. Among the more important of the adjuvants is a polyacrylate which has been found to be useful in
- 40 controlling bead characteristics and bulk density, has dispersing, anti-deposition and anti-redeposition effects in the present compositions, and aids in maintaining the crutcher mix fluid and homogeneous.
- 45 The polyacrylate, present in preferred base beads of this invention, is a low molecular weight polyacrylate, such molecular weight usually being within the range of about 1,000 to 5,000 preferably 1,000 to 3,000, and most preferably
- 50 1,000 to 2,000 or about 2,000. The polyacrylate may be partially neutralized or completely neutralized, e.g., about 1/2 or 1/3 present as sodium polyacrylate. Although modified polyacrylates may be substituted for the
- 55 described sodium polyacrylate, including some other alkali metal polyacrylates and hydroxylated polyacrylates, it is preferred that such substitutions be limited to a minor proportion of the material and preferably the polyacrylate will
- 60 be an unsubstituted sodium polyacrylate. Such materials are available from Alco Chemical Corporation under the name of Alcosperse (Registered trade mark). The sodium polyacrylates are available as clear amber liquids or powders,
- 65 with their solutions being of about 25 to 40%

- solids content, e.g., 30%, and with the pH of such solutions or of a 30% aqueous solution of the powder being in the range of about 7.5 to 9.5, e.g., about 9. Such materials are completely
- 70 soluble in water and have been employed as dispersants. They have been shown to possess the capability of binding calcium ions and have been used to prevent depositing out of insoluble calcium compounds from aqueous solutions. In
- 75 the present spray drying process small quantities (or percentages) thereof help to make the resulting beads of improved porosity.
- When the crutcher mix includes carbonate and/or bicarbonate and silicate, even if the
- 80 amount of the silicate is small, there may be a tendency for the mix to gel or "freeze" in the crutcher, especially if, due to delays in processing, the crutcher mix is held longer than the normal 30 minutes or so. In such cases, when silicate is
- 85 present processing aids are preferably also present in the mix (and consequently, in the finished base beads and detergent composition) to prevent premature solidification or gelation. Most preferably, such include citric acid and
- 90 magnesium sulphate. Instead of citric acid, soluble citrates, such as sodium citrate, may be used and while it is preferable to employ anhydrous magnesium sulphate, various hydrates thereof, such as epsom salts, may also be used.
- 95 Also, magnesium citrate can be used instead. The use of magnesium and citrate ions forms the subject matter of our copending British patent application No. 8129188. In place of the preferred antigelling system other means and suitable
- 100 systems for maintaining the crutcher mix fluid may be substituted, such as sodium sesquicarbonate, employed in replacement of some of the sodium carbonate and sodium bicarbonate. The use of sodium sesquicarbonate
- 105 forms the subject matter of our copending British patent application No. 8131798. However, while such processing aids are useful in many cases, it is a feature of this invention that they are not needed in manufacturing the preferred base
- 110 beads from which silicate is omitted.
- Although some adjuvants, such as fluorescent brightener, pigment, e.g., ultramarine blue, titanium dioxide, and inorganic filler salt may be
- 115 added in the crutcher, others, such as perfumes, enzymes, bleaches, some colourants, bactericides, fungicides, fabric softeners and flow promoting agents may often be sprayed onto or otherwise
- 120 mixed with the base beads or spray dried detergent composition, with any nonionic detergent and/or independently, so that they will not be adversely affected by the elevated
- temperatures of the spray drying operation and also so that their presence in the spray dried beads does not inhibit absorption of nonionic
- 125 detergent, when such is to be post-sprayed onto the beads. However, for stable and normally solid adjuvants, mixing with the starting slurry in the crutcher is also feasible. Thus, it is contemplated that pigments and fluorescent brighteners, when
- 130 employed, will normally be present in the crutcher

mix from which the present base beads are sprayed. The preferred colouring agent is ultramarine blue but other stable pigments and dyes may be used with it or in replacement of it.

- 5 Because the spray dried base beads of this invention sometimes may be off-colour, usually due to employment of naturally occurring minerals, the hue from such colouring agent may be adversely affected. It has been found that
- 10 incorporating a small proportion of titanium dioxide in the crutcher mix helps to retain the desired hue of the colouring agent and the presence of the titanium dioxide does not appear to have any adverse effect on the appearance of
- 15 laundry washed with detergent compositions made from base beads containing it.

- Among the fluorescent brighteners the most preferred is Tinopal (Registered trade mark) 5BM, especially in extra concentrated form. However,
- 20 various other cotton brighteners, such as those sometimes referred to as CC/DAS brighteners, derived from the reaction product of cyanuric chloride and the disodium salt of diaminostilbene disulphonic acid, may also be employed, including
- 25 variations thereof with respect to substituents on the triazine and aromatic rings. This class of brighteners is known in the detergent art and will be used most often when bleaching components are not present in the final product. When it is
- 30 desired for the detergent composition to include a bleach, such as sodium perborate or other oxidizing bleach, bleach stable brighteners will usually be incorporated in the crutcher mix. Among these there may be mentioned the benzidine sulphone
- 35 disulphonic acids, naphthotriazolyl stilbene sulphonic acids and benzimidazolyl derivatives. Polyamide brighteners, which also may be present, include aminocoumarin or diphenyl
- 40 pyrazoline derivatives, and polyester brighteners which can also be used, include naphthotriazolyl stilbenes. Such brighteners are normally used as their soluble salts but they may be charged as the corresponding acids. The cotton brighteners will usually comprise major proportions of the
- 45 brightener systems employed.

- Enzyme preparations, which normally are post-added to the base beads because they are heat sensitive, may be any of a variety of commercially available products, included among which are
- 50 Alcalase (Registered trade mark), manufactured by Novo Industri, A/S, and Maxatase (Registered trade mark) both of which are alkaline proteases (subtilisin). Maxazyme (Registered trade mark) 375 is sometimes preferred. Although the alkaline
- 55 proteases are most frequently employed, amylolytic enzymes, such as alpha-amylase, may also be utilized. The mentioned compositions usually contain active enzymes in combination with an inert powdered vehicle, such as sodium or
- 60 calcium sulphate, and the proportion of active enzyme may vary widely, usually being from 2 to 80% of the commercial preparation. In this specification proportions referred to are of the enzyme preparations, not the active part thereof
- 65 only. Perfumes employed, which are usually heat

sensitive and may contain volatiles, including a solvent, such as alcohol, are normally of synthetic perfumery materials, sometimes mixed with natural components, and generally will include

70 alcohols, aldehydes, terpenes, fixatives and other normal perfume components. Flow promoting agents, such as special clays, which are sometimes added to detergent products, while often useful to improve flowability and to diminish

75 tackiness of various compositions, are unnecessary in the present case, possibly in part due to the presence of the bentonite and the absence or very limited presence of silicate. However, they may be added if desired, to further

80 increase flowability. While it has been found that detergent compositions made from the present base beads do not require the presence of any anti-corrosion additive to replace the omitted

85 silicate, it is within the scope of the present invention to utilize suitable such materials and it will be preferred to employ those which are stable under crutching and spray drying conditions and which do not adversely affect such operations. Such anti-corrosion additives or antioxidants may

90 be organic or inorganic, with inorganic materials normally being preferred, and they will preferably be chosen for suitability for preventing corrosion of aluminium parts of washing machines. If it is desired to continue to utilize a silicate for such

95 purpose or to employ a silicate for its magnesium ion hardness treatment effect, a powdered silicate will normally be preferable, such as hydrous sodium silicate, which is commercially available under the name Britesil (Registered Trade Mark)

100 manufactured by Philadelphia Quartz Co. ($\text{Na}_2\text{O}:\text{SiO}_2=1:2.4$), and such will preferably be post-added. However, other normally solid soluble silicates, preferably of alkali metals, may also be post-added to the beads of this invention,

105 preferably after any absorption of nonionic detergent that is to be effected.

- When it is desired for the product which is made to possess textile softening characteristics, softening materials preferably in dry powder form,
- 110 may also be post-added to the base beads in suitable manner. This class of materials is well known and most generally such softeners are cationic compounds particularly quaternary ammonium compounds, such as quaternary ammonium halides. Especially preferred are the
- 115 higher alkyl-, alkylaryl- and arylalkyl-lower alkyl quaternary ammonium chlorides and bromides, such as distearyl dimethyl ammonium chloride. Of commercial softening materials that which is most preferred is sold under the trade name
- 120 Arosurf (Registered trade mark) TA-100, manufactured by Sherex Chemical Company, Inc. Such compounds possess antistatic and antibacterial properties too but if desired, other
- 125 antibacterial adjuvants may also be employed, preferably also incorporated in the product by post-addition.

- Of course, water is present in the crutcher to serve as the medium for dispersing the various
- 130 other bead components, and some water, in both

free and hydrate form, is in the product. During drying of the beads the initial moisture content thereof, which will be about 25 to 60% may be lowered to about 5 to 15% with such moisture content being sufficient so that the bentonite in the dried beads contains at least 2% and preferably at least 4% of moisture. It is preferred to employ deionized water, so that the hardness ion contents thereof may be very low and so that metallic ions that can promote decomposition of any organic materials which may be present in the crutcher mix, base beads and detergent are minimized, but city or tap water may usually be employed instead. Normally the hardness content of such water will be less than 150 p.p.m., as calcium carbonate (CaCO_3), more preferably the hardness content will be less than 100 p.p.m. and most preferably it will be less than 50 p.p.m.

The proportions of the various components in the base beads and in the spray dried detergent composition beads will be such as to result in them being free flowing and, for the base beads, sufficiently absorptive of a nonionic detergent applied thereto in liquid state so that the detergent compositions will be satisfactorily free-flowing. Also, of course, the detergent compositions will be effective cleaning agents, with the builders present acting to assist the organic detergent in its deterative effect in aqueous solutions of the compositions, and it is important that the resulting products be such that they do not cause objectionable depositions of zeolite particles (or zeolite-silicate aggregates) on washed materials. The zeolite particles and the bentonite particles, although insoluble, will not objectionably discolour or lighten coloured laundry as charged, because of their small particle sizes, but such discolouration can occur when zeolite aggregates are formed which are sufficiently large so as to be held to fabrics and also to be readily noticeable to the eye, especially when substantial proportions thereof are not removed from the laundered materials by being exhausted with the drying air during automatic drying. It is also desirable for the base beads and detergent composition beads made to be of appropriate bulk density and colour.

It has been found that satisfactory beads to accomplish the aforementioned purposes comprise by weight from 5 to 60% of water softening aluminosilicate (zeolite), 2 to 40% of bentonite (of the desired moisture content) and 5 to 60% of water soluble builder or mixture of such builders. From 0 to 30% of water soluble synthetic organic detergent and/or from 0 to 5% of water soluble silicate may also be present but often are preferably omitted. Preferably, the spray dried beads will contain from 3 to 15% of moisture, more preferably from 5 to 12% thereof and usually from 7 to 10% thereof, including any water of hydration present. Such water of hydration may be present in the zeolite, NTA, phosphate, carbonate, bicarbonate or magnesium sulphate or any or all of such materials, when such are in the formula, in addition to that

between the plates of the bentonite. The recited moisture content includes even strongly held water of hydration, such as that still retained by the zeolite even after several hours of distillation of a toluene dispersion. In some instances, as when the concentration of zeolite in the product is high, so that up to about 12 to 15% of moisture could be present in the zeolite as water of hydration, the moisture content in the spray dried beads may be as high as 20% and occasionally, may go up to about 25%. Normally, however, for good flowability of the product and to minimize tackiness and lumping, such upper limit will be about 15%, especially when the final detergent composition contains an appreciable proportion of nonionic detergent. The percentage of zeolite given includes the water of hydration therein. It is possible to make useful spray dried beads of moisture contents less than 3% providing that the bentonite has sufficient water associated with it, for the reasons previously given but due to the strong attraction for moisture of the zeolite and due to the actions of the other hydratable materials that may be present it has usually been found that a minimum of 3% of moisture is needed to avoid loss of the desired internal moisture of the bentonite, which appears to "lubricate" the plates and facilitate their separation when a product containing them is dispersed in water. Also, when anhydrous products are made, even when sufficient moisture is retained in the bentonite, they are liable to be physically unstable, powdering more readily and being subject to attrition and disintegration.

The bulk density of the spray dried beads may be within the range of 0.2 to 0.9 gr/cc. Bulk densities in the lower part of this range are more readily obtainable when there is no silicate in the crutcher mix being spray dried and when little or no nonionic detergent is absorbed by the beads. The higher bulk densities result when nonionic detergent is applied to porous beads and when some silicate is present in the beads. Such lighter products have bulk densities in the 0.2 to 0.5 gr/cc. range, often 0.3 to 0.4 gr/cc., and the heavier particles are of bulk densities in the 0.6 to 0.9 gr/cc. range, usually 0.6 to 0.8 gr/cc. The bead particle sizes will usually be in the range of No's. 10 to 100 (through No. 10 and on No. 100), U.S. Sieve Series, more preferably 10 to 60, U.S. Sieve Series. 100 U.S. mesh base openings of 149 microns, 10 mesh has openings of 2000 microns (2 mms) and 60 mesh has openings of 250 microns. In preferred formulations the proportion of bentonite to zeolite is in the range of 1:4 to 1:1, the proportion of water soluble builder to zeolite is within the range of 1:2 to 3:1 and the proportion of bentonite to water soluble builder is within the range of 1:10 to 1:1. More preferably, such ranges of ratios are 1:3 to 2:3, 2:3 to 2:1, and 1:6 to 1:2, respectively. Percentagewise, the compositions preferably comprise from 10 to 40% of a partially hydrated sodium zeolite, preferably containing from 15 to 25% by weight thereof water of hydration and with an

exchange capacity for calcium ion in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, 2 to 35% of bentonite, which is of a

- 5 type which has a swelling capacity in the range of 7 to 15 ml/gr and is of viscosity in the range of 8 to 30 centipoise at 6% concentration of water, 10 to 50% of water soluble alkali metal builder salt or mixture
10 thereof, 0 to 25% of water soluble synthetic, preferably anionic, organic detergent and 0 to 3% of water soluble silicate, which silicate, when present, is an alkali metal silicate of alkali metal oxide: silicon dioxide ratio in the
15 range of 1:1.6 to 1:3, more preferably 1:2 to 1:2.8. More preferred bead formulas include 15 to 35% of zeolite A, 5 to 20% of beneficiated Wyoming bentonite, 20 to 50% of water soluble sodium builder salt or mixture thereof, 0 to 20%
20 of water soluble synthetic, preferably anionic, organic detergent and 0% of sodium silicate.

Although carbonate and bicarbonate builders are useful in making base beads within this invention, especially those onto which nonionic

- 25 detergent is to be sprayed, polyphosphate and/or nitrilotriacetate builders are often preferred for the spray dried beads, whether such include anionic detergent or not, and whether or not intended to have nonionic detergent applied to them.
30 Preferred formulas of base beads based on NTA as the sole or main soluble builder include from 15 to 35 or 40% of hydrated zeolite, 5 or 10 to 20% of bentonite, and 20 to 50 or 60% of NTA. When a phosphate, such as sodium tripoly-
35 phosphate, is to be the principal or basic water soluble builder, the same proportions of zeolite and bentonite may be employed, but usually more phosphate can be present (than NTA). Preferably, for such base beads onto which nonionic
40 detergent is to be sprayed or for comparable compositions based on carbonate or a mixture of bicarbonate and carbonate (with the ratio of carbonate: bicarbonate in the spray dried beads being within the range of about 1:1 to 3:1), there
45 will be no water soluble synthetic organic detergent and little or no water soluble silicate present. When bicarbonate and carbonate together are employed in such formulations they will usually total from 20 to 40% of the base
50 beads and when carbonate alone is employed it will normally be 10 to 30% thereof.

When an anionic detergent or other suitable organic detergent is included in the crutcher so as to produce a spray dried detergent product

- 55 preferred proportions thereof will be 3 or 5 to 30%, more preferably 5 to 25%, and most preferably 10 to 25%, e.g., 10%, 15% of such product, and the detergent will preferably be selected from the group consisting of sodium
60 linear alkyl benzene sulphate wherein the alkyl group is of 10 to 18 carbon atoms, sodium fatty alcohol sulphate wherein the alcohol is from 10 to 18 carbon atoms and sodium fatty alcohol ethoxylate sulphate wherein the fatty alcohol is of
65 10 to 18 carbon atoms and which contains from

3 to 30 ethylene oxide groups per mole, and mixtures thereof. At present, the most preferred of the detergents is sodium linear tridecyl benzene sulphonate, and the alkyl groups are preferably of
70 12 to 16 carbon atoms.

When polyacrylate is present in any of the detergent compositions or base beads it will normally be from 0.05 to 1% thereof and its molecular weight is preferably within the range of
75 1,000 to 5,000.

- Because the presence of anionic detergent in the spray dried detergent beads may inhibit the production of a bead structure which will be absorptive of a desired proportion of nonionic detergent it may be preferred to produce spray
80 dried detergent beads of a type within this invention and mix them with base beads according to the present invention onto which nonionic detergent has been sprayed, so that a higher proportion of nonionic detergent may be present in the finished product. To do this varying ranges of proportions may be employed e.g., 1:10 to 10:1, 1:5 to 5:1 and 1:2 to 2:1 of the mentioned components, depending on the
85 characteristics wanted in the final product. It will be desirable for the bulk densities of the beads before mixing to be approximately the same, preferably within 0.1 gr/cc. of each other and the particle sizes should be approximately the same, normally being within the No. 10 to 100, U.S. Sieve Series range, to prevent sifting and separation of the final mix.
90

- Proportions of adjuvants and processing aids in the base beads and spray dried detergent will
100 normally be limited to 20% thereof, preferably being 1 to 10% and more preferably being 3 to 7% thereof. The proportions of processing aids, when magnesium sulphate and citric acid are employed, will normally be from 0.5 to 2% of
105 magnesium sulphate, preferably 1 to 5% thereof, and 0.1 to 0.5% of sodium citrate, preferably 0.1 to 0.3% thereof. With respect to colouring, pigmenting and fluorescent brightening agents, when present, the proportions will normally be
110 from 0.05 to 0.6% of colouring pigment, such as ultramarine blue, preferably 0.2 to 0.4%, and 0.1 to 4% of fluorescent brightener, preferably 1 to 3% thereof. The proportion of titanium dioxide (a whitening pigment) will normally be from 1 to 3%,
115 preferably 1.5 to 2.5%. If a colouring dye or dyes are used instead of a colouring pigment, proportions will usually be 1 to 50%, especially 5 to 20% of those of the colouring pigments.

- For preferred spray dried beads within this
120 invention, which may contain NTA or polyphosphate builders with or without synthetic organic detergent, or may contain such detergent with any of a previously given list of preferred water soluble builder salts, the bulk density is in
125 the range of 0.2 to 0.8 gr/cc., the aluminosilicate is hydrated zeolite A, the bentonite includes at least 3% moisture on an anhydrous bentonite basis, the water soluble silicate, if present, is sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of
130 1:2 to 1:2.8, and the moisture content of the

beads is from 3 to 12% thereof. When the beads contain NTA or other sodium salt of nitrilotriacetic acid, with or without synthetic organic detergent, the proportion of bentonite:zeolite is in the range of 1:6 to 1:2 that of NTA:zeolite is in the range of 1:2 to 2:1, and that of bentonite:NTA is in the range of 1:6 to 1:2, and the percentages of hydrated zeolite, bentonite, sodium nitrilotriacetate, and silicate are respectively, within the ranges of 10 to 40%, 2 to 25%, 10 to 40%, and 0 to 5%.

When preferred NTA-containing beads also contain a synthetic anionic organic detergent, with the aforementioned zeolite A, bentonite and moisture, and with or without soluble silicate, they preferably comprise 5 to 30% of synthetic anionic organic detergent, which will be sodium linear alkyl benzene sulphonate wherein the alkyl group is of 10 to 18 carbon atoms, sodium fatty alcohol sulphate wherein the alcohol is of 10 to 18 carbon atoms, or sodium fatty alcohol ethoxylate sulphate wherein the fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 30 ethylene oxide groups per mole, or a mixture comprising two or more thereof, the water soluble builder is a sodium salt of nitrilotriacetic acid (NTA), the proportion of bentonite: zeolite is in the range of 1:6 to 1:1, that of NTA:zeolite is in the range of 1:3 to 3:1, that of bentonite:NTA is in the range of 1:10 to 1:1, and that of synthetic anionic organic detergent:zeolite is in the range of 1:1 to 1:4, and the percentages of hydrated zeolite, bentonite, sodium nitrilotriacetate, synthetic anionic organic detergent, and silicate are respectively, within the ranges of 10 to 40%, 2 to 25%, 10 to 40%, or 10 to 25% (a more preferred range), and 0 to 5%.

For phosphate-containing beads, with or without the synthetic detergent the materials and ratios are the same as for the corresponding NTA-containing beads, with pentasodium tri-polyphosphate or tetrasodium pyrophosphate or a mixture thereof substituted for NTA, but the percentages are within the ranges of 15 to 35%, 5 to 20%, 15 to 40% and 0 to 5%, respectively, instead. Similarly, for the phosphate-containing beads with anionic detergent also present, the materials and ratios are the same as for the corresponding NTA-containing beads and the percentage ranges are the same except for that for total polyphosphate, which is 10 to 50%.

The ranges of proportions of the various base bead components in the final detergent composition, when nonionic detergent (possibly with other materials) is post-added may readily be calculated from those given for the base beads, diminished by proportions of the detergent and other materials that are post-added to the beads. Conversely, the bead component proportions (and from them the crutcher mix formula) may be calculated back from the final product formulation. Thus, for example, calculating the final product formula ranges from the bead ranges, if the final detergent composition had only nonionic detergent added to it so that the final

product contains 20% of nonionic detergent, from the various ranges given for components in the base beads ranges of proportions thereof in the final detergent composition product may be calculated by multiplying by 0.8, which is (100-20)/100. Similarly, when the proportion of nonionic detergent (in formulas wherein it is the only additive to the beads) may range from 8 to 25% of the detergent composition, the multipliers will be from 0.92 to 0.75. The final percentage of nonionic detergent in the product will be in the 8 to 30% range, preferably being 10 to 25% and more preferably being 15 to 22%, e.g. about 20%, but in some situations, for certain types of products, proportions in the 8 to 13% range may be preferred. Normally, the percentage of perfume in the final product will be in the range of 0.1 to 1%, preferably 0.2 to 0.4%, the percentage of enzyme will be from 0.5 to 3%, preferably 1 to 2%, and if a hydrous sodium silicate is to be post-added the proportion thereof will usually be no less than 1% and is preferably limited to about 5%, although in some cases as much as 10% has been used. When a softening compound is present in the final product the proportion thereof will normally be in the range of 3 to 12%, preferably 5 to 10%.

The base beads and the spray dried detergent beads of the invention are spray dried from an aqueous crutcher mix which normally will contain from about 40 to about 70 or 75% of solids, preferably 50 to 65% thereof, with the balance being water, preferably deionized water, as previously described (but city water may also be employed). The crutcher mix is preferably made by sequentially adding various components thereof in a manner which will result in the most miscible, readily pumpable and non-setting slurry for spray drying. The order of addition of the materials may be varied, depending on the circumstances, but it is highly desirable to add the silicate solution (if any) last, and if not last, at least after the addition of any gel or "Freeze"-preventing combination of materials or processing aids, such as citric acid and magnesium sulphate. Normally it is preferable for all or almost all of the water to be added to the crutcher first, preferably at about the processing temperature after which the processing aids (if present) and other minor components, including pigment, and fluorescent brightener and polyacrylate, if present, are added, followed by the zeolite, water soluble builder, anionic detergent (if present), bentonite and silicate (if present). Usually during such additions each component will be mixed in thoroughly before addition of the next component but methods of addition may be varied, depending on the circumstances, so as to allow co-additions when such are feasible. Sometimes component additions may be in two or more parts and sometimes different components may be pre-mixed before addition, to speed the mixing process. Normally, mixing speed and power will be increased as the materials are added. For example, low speeds may be used until after

admixing in of the last of the zeolite or soluble builder, after which the speed may be increased to medium and then to high, at which it will preferably be before, during and after addition of any silicate solution.

The temperature of the aqueous medium in the crutcher will usually be about room temperature or elevated, normally being in the 20 to 80°C range, preferably from 30 to 75 or 80°C, and more preferably 40 to 70°C. Heating the crutcher medium may promote solution of the water soluble salts of the mix and thereby increase miscibility but the heating operation, when effected in the crutcher, can slow production rates and can sometimes promote setting of the mix.

An advantage of having processing aiding materials present in the mix (especially if any soluble silicate is present) is that they ensure that at higher and lower temperatures non-gelling slurries will result. Temperatures higher than 80°C (and sometimes those higher than 70°C) will usually be avoided because of the possibility of decomposition of one or more of the crutcher mix components e.g., sodium bicarbonate. Also, in some cases lower crutcher temperatures increase the upper limits of crutcher solids contents, probably due to insolubilizing of normally gelling or setting components.

Crutcher mixing times to obtain good slurries can vary widely, from as little as five minutes in small crutchers and for slurries of higher moisture contents, to as much as four hours, in some cases. The mixing times needed to bring all the crutcher mix components substantially homogeneously together in one medium may be as little as ten minutes but in some cases can take up to one hour, although 30 minutes is a preferable upper limit. Counting any such initial admixing times, normally crutching periods will be from 15 minutes to two hours, e.g., 20 minutes to one hour, but the crutcher mix should be such as to be mobile, not gelled or set, for at least one hour, preferably for two hours, and more preferably for four hours or longer after completion of the making of the mix, and preferably will be mobile for as long as 10 to 30 hours before pump-out to the spray tower, to allow for situations wherein other manufacturing problems may be encountered.

The crutched slurry, with the various salts and any other components thereof dissolved or in particulate form, uniformly distributed therein, is transferred in usual manner to a spray drying tower, which is normally located near the crutcher. The slurry is dropped from the bottom of the crutcher to a positive displacement pump, which forces it at high pressure through spray nozzles at the top of a conventional spray tower (countercurrent or concurrent) wherein the droplets of the slurry fall through a hot drying gas, usually the combustion products of fuel oil or natural gas, in which the droplets are dried to desired bead form. During the drying, part of the bicarbonate (if present) may be converted to carbonate, with the release of carbon dioxide,

which, in conjunction with any of the polyacrylate present in the mix being spray dried, improves the physical characteristics of the beads made, so that they become more absorptive of liquids, such as liquid nonionic detergent, which may be post-sprayed onto them subsequently. However, the zeolite, bentonite and polyphosphate (when present) components of the base beads made also appear to favour absorption of liquid and the production of a strong bead, and the polyacrylate improves bead characteristics and promotes faster drying, thereby increasing tower throughput.

After drying, the product is screened to desired size, e.g., 10 to 60 or 100, U.S. Sieve Series, 100 U.S. mesh has openings of 149 microns, 10 mesh has openings of 2000 microns (2 mms) and 60 mesh has openings of 250 microns, and is ready for application of nonionic detergent spray thereto, if it is a base bead formula, with the beads being either in warm or cooled (to room temperature) condition. However, the nonionic detergent will usually be at an elevated temperature, such as 30 to 60°C, e.g., 50°C, to ensure that it will be liquid; yet, upon cooling to room temperature, it will desirably be solid, often resembling a waxy solid. Even if at room temperature the nonionic detergent is somewhat tacky, this characteristic does not make the final composition poorly flowing because the detergent penetrates to below (or within) the bead surface. The nonionic detergent is preferably applied to the beads whilst they are moved or tumbled e.g. in known manner, as a spray or as droplets. The nonionic detergent is preferably a condensation product of ethylene oxide and higher fatty alcohol, such as was previously described, but other nonionics may also be operative. The enzyme preparation (herein referred to as an enzyme, although it is recognised that it includes a carrier material, too), hydrous silicate and any other powdered adjuvants may be dusted onto the detergent particles, and perfume and any other liquids to be post-added may be sprayed on at a suitable point before or after addition(s) of the powder(s).

The spray dried detergent, the spray dried base beads and the detergent compositions made from them include little or no silicate from the crutcher mix, although some silicate in solid form may be post-added. The post-added powdered silicate, if employed, does not seem to react with the zeolite as much, as zeolite-silicate agglomerations that tend to deposit on laundered articles are reduced, compared to such deposits from products wherein silicate was added in the crutcher. Although, without the bentonite being present, silicate would normally be used for its bead controlling and anti-corrosion effects, the present detergent compositions produce acceptable beads and have not been found to cause the corrosion of aluminium articles. Furthermore, the bentonite does not adversely affect the stability of the product and in fact, appears to help to hold the beads together,

making them resistant to crushing and powdering during shipment and use. The presence of the bentonite significantly improves the properties of the final detergent composition, resulting in

5 higher calcium ion binding rates and in less zeolite being deposited on laundered fabrics. When the low molecular weight polyacrylate is present the base beads become more porous and better absorb the nonionic detergent in liquid state,

10 without unduly lowering the bulk density of the product. Considering that bentonite is a clay and serves as a binder, it might be expected to create deposition and gelation problems of its own. Therefore, the lowered deposition characteristics,

15 absence of gelation, and ready product dispersion are surprising, and they are important results of the present invention. Also considered to be important results of the presence of the small proportion of polyacrylate in the spray dried beads

20 is the improved spray drying of the present base beads and detergent compositions, and the improved sorption of liquid nonionic detergent by the base beads.

The present invention may be put into practice

25 in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples some of which are comparative. Unless otherwise indicated, all temperatures are in °C and

30 all parts are by weight in the examples and throughout the specification. When weights and proportions of zeolite are given, these are intended to be for the normal hydrate being used, because it is considered that the zeolite water of

35 hydration does not leave the zeolite and does not become part of the aqueous solvent medium in the present crutching operations. Also, part of the water present in the base beads and the detergent compositions is present as water of

40 hydration of the zeolite. Similarly, the moisture associated with the bentonite may also be considered not to be free moisture but because of the lesser percentage present, this distinction can often be neglected, as a practical matter.

45 Examples 1A to 1C

Example 1A

A 100 parts batch of crutcher mix for spray drying base beads considered as satisfactory for subsequent conversion to a detergent

50 composition by addition of synthetic nonionic organic detergent thereto was made by adding to the crutcher 47 parts of deionized water at a temperature of about 27°C (80°F), and then sequentially, and initially with low speed crutcher

55 mixing, admixing with it 1.04 parts of Tinopal (Registered trade mark) 5 BM Extra Conc. (CIBA-Geigy), 0.13 part of ultramarine blue powder, 0.07 part of sodium polyacrylate (Alcosperse (Registered trade mark) 107D) 21.11 parts of

60 Linde (Registered trade mark) hydrated zeolite 4A (20% water of crystallization), 6.25 parts of Mineral Colloid No. 1 (bentonite), 15.75 parts of sodium bicarbonate (industrial grade), 7.74 parts

of sodium carbonate (natural soda ash) and 0.91

65 part of titanium dioxide (anatase). During mixing of the various components the mixer speed was increased to medium and ultimately to high and after addition of all the constituents, which took approximately fifteen minutes, mixing was

70 continued for about an hour (in some cases as long as four hours of mixing may occur) during which time some of the water present e.g., about two to six parts, may be lost by evaporation, and may be replenished, if desired. During the mixing

75 time the crutcher slurry was continuously mobile and did not gel, set or cake. Because bicarbonate partially decomposes to carbonate during spray drying, the amounts of bicarbonate and carbonate in the crutcher formulation may be varied,

80 depending on the spray tower operating characteristics.

Starting about five minutes after all the components of the crutcher mix were present, the mix was dropped from the crutcher to a pump,

85 which pumped it at a pressure of about 21 kg/sq cm into the top of a counter-current spray tower wherein the initial temperature was about 430°C, and the final temperature was about 105°C. The essentially inorganic base beads resulting were of

90 a bulk density of about 0.6 to 0.7 gr/cc, percentage initial adhesion less than 10%, a particle size range substantially between 10 and 60 mesh, U.S. Sieve Series (they were screened to such range), and a fines characteristic (through

95 U.S. Sieve No. 50 which has openings of 297 microns) of about 15%. The moisture content of the beads was in the range of 1 to 10%, normally being closer to 10%, e.g., 8 to 10%. The base beads were found to be free flowing (80% flow index), non-tacky, satisfactorily porous, yet firm

100 on the surfaces thereof. They were capable of readily absorbing significant proportions of liquid nonionic detergent without becoming objectionably tacky.

105 Example 1B

Detergent products were made from the spray dried beads by spraying onto the tumbling bead surfaces thereof a normally waxy nonionic detergent. Neodol 23-6.5 was used but Neodol

110 23-7 or Neodol 25-7 (and sometimes Neodol 45-11) may be substituted. The nonionic detergent was in heated liquid state (at a temperature of about 45°C). The quantity sprayed was such as to result in a final product containing about 20% of

115 nonionic detergent. Proteolytic enzyme (alcalase 1.7T or Maxazyme 375) was applied in powdered form to result in about a 1.5% concentration (of the commercial composition) in the product, and perfume is sprayed onto the product to produce a

120 0.25% concentration therein. The resulting detergent compositions are of a bulk density of about 0.7 to 0.8 gr/cc and contain about 32.45% of zeolite (hydrated), 19.7% of the nonionic detergent, 18.5% of sodium carbonate (some of which was produced by decomposition of sodium bicarbonate), 13.5% of sodium

125 bicarbonate, 1.3% of free water, 1.4% of enzyme,

1.6% of fluorescent brightener, 0.25% of perfume, 0.2% of ultramarine blue, 9.6% of bentonite, 0.1% of sodium polyacrylate and 1.4% of titanium dioxide.

- 5 The detergent so made, of the above formula, was an excellent heavy duty laundry detergent and was especially useful for washing household laundry in automatic washing machines. It was physically and aesthetically advantageous and attractive because it was non-dusting and extremely freely flowing, which allowed it to be packaged in a narrow-necked glass and plastic bottles, from which is flowed readily for dispensing. The detergent compositions produced, containing bentonite, as described, are of improved calcium ion binding rates but more importantly, they leave less zeolite residue on laundry washed with them (in an automatic washing machine at usual concentrations for such products and at normal wash temperatures), especially when such laundry is line dried, than so similar compositions containing less bentonite and with sodium silicate in the spray dried base beads. This difference is accentuated when the wash water is high in hardness, e.g., 200 p.p.m., as calcium carbonate, the wash water is cold, and a gentle agitation cycle is employed.

- 10 The base beads and detergent composition made are acceptable standards against which the other described beads and detergent compositions of the following examples may be measured, and to which they compare favourably. Also, the manufacturing methods are essentially the same and are considered to be satisfactory.

- 15 Following normal procedure, crutcher mixes will be made quickly and may be emptied from the crutcher equally fast, sometimes being made within a period of as little as five minutes and being pumped out of the crutcher in as little as ten minutes. Yet, it is often important that the present mixes be able to withstand at least an hour in the crutcher without gelling or solidifying because sometimes holdups of such lengths of time are encountered in commercial production.
- 20 The described crutcher mix is capable of being held for as long as four hours, and often appreciably longer, without gelling or solidifying, which is attributed, at least in part, to the content of bentonite and the absence of silicate. This action of the bentonite is unexpected because it also has a thickening effect on the crutcher mix, but although the mix may thicken appreciably it remains pumpable. Minor components of the crutcher mix, such as the fluorescent brightener and pigment, may be omitted therefrom and enzyme and perfume may be omitted from the final product, although it is highly preferable for all such materials to be present. The crutcher mix temperature may be modified, as by elevation to 52°C, and the proportions of the various components may be varied by $\pm 10\%$, $\pm 20\%$ or $\pm 30\%$, while still maintaining them within the ranges previously given, and workable mixes that result in the desired beads and detergent compositions will be obtainable. The crutcher mix

- solids contents may be varied over the range recited, e.g., to 45% and 65%, and good mixing and spray drying result. Other orders of addition to the crutcher of components may be employed but normally it will be desired to add any silicate last or near the end, and it is preferred that the bentonite also be added late in the process, preferably just before the silicate. Instead of using Zeolite 4A, Zeolites X and Y may be substituted, as may be other types of Zeolite A. While it is preferred to employ the approximately 80% hydrated Zeolite 4A (about 20% moisture content) of this example, various degrees of hydration of the zeolite are acceptable and in some instances nearly anhydrous crystalline zeolites or amorphous zeolites may be employed. Varying the amount of bentonite within the range given to 7%, 13% and 19% in the base bead, for example, still results in useful products, but those containing the larger proportions of bentonite will usually be more effective in helping to prevent zeolite deposition on laundry. In some instances it may be desirable to utilize even higher percentages of bentonite, within the ranges set forth in this specification, taking care that the other components of the base bead will be such that the beads will be free flowing and effective detergents. The proportion of bentonite suitable to be employed commercially depends on a number of factors and normally will represent a balance struck between the desired diminution of zeolite residue and the desired building and other functional effects of other detergent composition components that could be incorporated in place of an increased amount of bentonite.

Example 1C

- The improvement noted in the detergent compositions of this example depositing less residue on washed laundry was verified by testing the described product (Example 1B) against a control product (Example 1C) of essentially the same formula, with no bentonite present and containing about 8% of sodium silicate in the final product. In this evaluation a Whirlpool Suds Saver model washing machine was employed, with the washing periods being eight minutes at a gentle wash cycle. The detergent composition concentration was 0.06%, the wash water was of mixed calcium and magnesium hardness with a total of 200 p.p.m. hardness, as calcium carbonate, and the water temperature was 24°C. The items washed were 100% cotton; 100% polyester- 85% acetate and 15% nylon; and 65% polyester and 35% cotton. The wash was observed wet and after line drying (line drying usually results in more visible residue than does automatic dryer drying). No residue was observed in either such case with the product of Example 1B. When the control formula detergent composition of Example 1C was tested, moderate residue was observed on all washed specimens.

The results of the practical residue test described above were verified by weighing the residue deposited on a denim test material. In

such test, the detergent composition of this invention (Example 1B) was filtered through a sample of denim material, with the detergent being in solution-suspension at 0.12%

- 5 concentration in 200 p.p.m. (as CaCO_3) hardness water at 24°C , and the weight of residue on the cloth was noted, and compared. By such test the percentage of residue for Example 1B compared to the control (Example 1C) was about 75%,
10 which is considered to represent a significant difference in the appearance of the washed products.

- The property of initial adhesion previously referred to, which measures tackiness of
15 detergent product, is tested as follows: 10 grams of base beads (or detergent composition, in some cases) are placed evenly between two watch glasses, both of which are 23 cm. in diameter, with a weight of 500 grams on top of the upper
20 watch glass (both watch glasses being concave side up). After standing there five minutes, the weight and top watch glass are removed and the bottom watch glass is inverted after which the product remaining stuck to such watch glass is
25 weighted. The percentage initial adhesion is the number of grams of product remaining on such watch glass multiplied by 10.

- The flow index of the product is determined by the following flow test. In this flow test the
30 volumetric flow rates of base beads (and in some cases final product) and standardized Ottawa sand ($-20+60$, U.S. Sieve Series) are compared by measuring the times required for complete emptying of a 1.9 litre Mason jar through a 2.2
35 cm. diameter circular hole in a nozzle attached to the cap thereof. The flow index % is the time for the sand flow divided by the time for the test product flow, times 100.

Examples 2A to 2D

40 Example 2A

- Base beads like those of Example 1 but with NTA included therein in place of some of the carbonate and bicarbonate were made by essentially the same method described in that
45 example. The formula was changed only by replacing 5 parts of the zeolite, 12 parts of the sodium bicarbonate and 3 parts of the sodium carbonate in the crutcher with 20 parts of NTA, as the trisodium salt monohydrate. The NTA was
50 added after the sodium carbonate during the mixing operation. The base beads obtained were not as crisp as those of Example 1 but were sufficiently satisfactorily free flowing. Instead of the final detergent composition containing 19.7%
55 of the nonionic detergent, it contained 12%, with the final percentages of the other components being increased accordingly. The resulting product was a satisfactory heavy duty particulate detergent.

60 Example 2B

In a variation of this formula, 2.5% of hydrous sodium silicate was post-added to the product for

its anti-corrosion properties and for its utility in tying up magnesium ions in the wash water.

- 65 Providing that the silicate was of about the same particle size and density it did not sift or segregate from the other detergent bead components during shipping and storage, and the resulting product met the specifications for a heavy duty
70 commercial detergent, but a small proportion of zeolite-silicate aggregate may be noted on washed materials.

Examples 2C and 2D

- In another alternative formula, 3% of sodium
75 silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of about 1:2.4 was included in the final product by addition of an aqueous solution thereof in the crutcher (Example 2C) together with 1.5% of magnesium sulphate and 0.4% of citric acid to prevent gelation or
80 setting in the crutcher. The finished product was a good heavy duty detergent but did deposit more zeolite-silicate aggregate on washed materials that were line dried than did a comparable formula (Example 2D) to which the hydrous
85 sodium silicate was post-added.

Examples 3A to 3F

- The procedure of Examples 2A to 2D were repeated but with pentasodium tripolyphosphate being substituted for the NTA. The products
90 obtained were good detergents, of a bulk density of about 0.8 g./cc. (as are those of Example 2) but such densities may be varied by adjustment of spray tower conditions and formulas so as to be within the range of 0.7 to 0.9, and in some cases
95 the densities may be lowered to 0.3. With the post-added silicate (Example 3D) the densities may be slightly higher, especially for those in the lower portion of the range. The product is more free flowing than that of Example 2 but is about
100 equivalent to it in washing power.

Example 3E

- In the above formula and those of the previous examples an additional proportion of bentonite may be added in the crutcher to make products
105 containing 15% (or more) of the bentonite. Such products are even better in binding effects, dispersibility and other desirable properties attributable to the bentonite and are good detergent (and base bead) preparations.

110 Example 3F

Also, the tripolyphosphate may be replaced, either in whole or in part, e.g., $1/2$, by tetrasodium pyrophosphate, and similar good products result.

Examples 4A to 4C

115 Example 4A

- A final detergent product was made essentially be the method of Examples 1 and 2 containing 30 parts of the zeolite, 30 parts of NTA, 20 parts of the nonionic detergent, 10 parts of Bentonite, 5
120 parts of sodium carbonate, 5 parts of water and 1.3 parts of enzyme composition. This product

had a density of about 0.5 g./cc. and was satisfactory detergent.

Example 4B

- However, to improve flowability of the product of Example 4A it is desirable for the nonionic detergent content to be decreased to 15% and preferably to 12%.

Example 4C

- To increase the bulk density of the product of Example 4B to about 0.7, half of the bentonite was replaced by sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:2.4), added as the last component in the crutcher as a 47.5% aqueous solution, and 1.5 parts of magnesium sulphate and 0.4 part of citric acid were correspondingly added as anti-gelling agents earlier in the making of the crutcher mix. The resulting product was of about 0.7 g./cc. bulk density and could absorb about 20 parts of nonionic detergent without becoming tacky or of diminished flowability. While it deposited less zeolite-silicate agglomerate than formulations with conventional greater proportions of silicate present from crutcher additions the agglomerate could be detected on laundry washed with the product and line dried.

Example 5

- Instead of manufacturing base beads to which detergent is applied to form a detergent composition the composition may be spray dried directly from the crutcher with a suitable synthetic organic detergent being included in the crutcher mix. Using essentially the same procedures as described in Example 1, a crutcher mix was made which was spray dried to detergent beads containing 16 parts of linear tridecyl benzene sulphonate, 20 parts of the zeolite, 12.5 parts of bentonite, 15 parts of NTA, 10 parts of sodium carbonate and conventional adjuvants (colourant, fluorescent brightener). The bulk density of the spray dried product was in the 0.3 to 0.8 range, normally being in the lower portion of such range and sometimes being as low as 0.2 gr/cc. In the manufacturing process the organic detergent will normally be added after the water. Drying will usually be to a moisture content of about 8 to 12%. The resulting product preferably has about 3 parts of hydrous sodium silicate post-added, together with other normal adjuvants, such as enzyme and perfume. It was a satisfactory heavy duty detergent which did not deposit objectionable amounts of zeolite or zeolite-silicate aggregate on washed fabrics. Due to the presence of the bentonite the detergent appeared to disperse very quickly when added to the wash water and it is considered that at least in part this quick dispersibility, together with the presence of the bentonite, tends to inhibit zeolite deposition.

Example 6

- The procedure of Example 5 was followed but the NTA was replaced by an equal weight of soda

ash. Such product was also a satisfactory heavy duty detergent.

Example 7

65 Example 7A

- The procedure of Example 5 was followed but pentasodium tripolyphosphate was included in place of NTA. The product made was especially free flowing and was a good heavy duty synthetic organic detergent composition.

Example 7B

- Although when silicate is to be present it is preferred that it be post-added as a hydrous sodium silicate, up to 5 parts of silicate may be added in the crutcher, together with the appropriate proportions of magnesium sulphate and citric acid, as described in previous examples, and useful detergent compositions will result, although some zeolite-silicate deposition will occur.

Example 7C

- In addition to the convention materials which may be post-added, there may be added to the product of this example (and to the products of other examples), softening proportions of a cationic material, e.g. 8% of dimethyl distearyl ammonium chloride, an amphoteric detergent, e.g., 5% of Miranol (Registered trade mark) C_{12}M (1-carboxymethyl-1-carboxyethoxyethyl-2-cocimidazolinium betaine), or a bleach, e.g., 15% of sodium perborate (preferably activated). The additions of such materials will diminish the proportions of the other components in the final composition and thereby will change the properties of the compositions somewhat, sometimes requiring the use of more of the product in the wash water to obtain the same cleaning effect.

Example 7D

- In Examples 5—7 the linear tridecyl benzene sulphonate may be replaced with an equal weight of sodium lauryl sulphate or sodium lauryl polyethoxy sulphate (3 to 10 EtO) or mixtures of such materials in equal parts and the products obtained are also useful as detergent compositions. Similarly, instead of the NTA, carbonate, carbonate and bicarbonate, and polyphosphate, sodium citrate and/or sodium gluconate may be substituted, at least in part, e.g., 1/4, 1/2, and good detergents result.

Examples 8A to 8C

Example 8A

- The products of Example 1A and Example 7A (the primary products first described) were mixed in equal proportion to obtain a final product with the characteristics of both such constituent parts. Prior to mixing the materials to be mixed were both of approximately the same bulk density, about 0.5 g./cc. and of about the same particle

- sizes, in the No's. 10 to 60 range, U.S. Sieve Series, so as to prevent separation during shipping and storage. The mixed product was especially useful for the removal of both oil-based and clay-based soils on laundry, and was free flowing, stable and attractive.

Example 8C

- In the Example 7 materials used in Example A the anionic detergent may be changed from sodium alkylbenzene sulphonate to a sodium alpha-olefin sulphonate (14—15 carbon atoms in the olefin) or to a sodium paraffin sulphonate (12—15 carbon atoms in the paraffin) and the mixtures made will also be useful detergents.

15 Examples 9A and 9B

Example 9A

- Following substantially the procedure described in Example 1 a crutcher mix was made from 36.9 parts of water, 1.2 parts of fluorescent brightener (Tinopae 5 BM, extra concentrated) 0.1 part of ultramarine blue, 2.1 parts of magnesium sulphate (heptahydrate), 0.3 part of sodium citrate, 22.4 parts of zeolite 4A powder (partially hydrated, to about 20% moisture content), 20.9 parts of trisodium nitrilotriacetate monohydrate, 7.4 parts of a 47.5% solids solution of sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:2.4$) 2.7 parts of sodium bentonite (formerly marketed at THIXO-Jel No. 2), 2.8 parts of natural soda ash and 2.1 parts of a mineral type compound, which may act to increase bead porosity, and as a building agent. The crutcher mix was spray dried in a manner like that previously described, with the moisture loss in drying being about 45.2%.

35 Example 9B

- Onto 78.4 parts of the spray dried base beads, of particle sizes in the No. 10 to 100 range (screened), were sprayed 20 parts of neodol 23—6.5, after which the beads were mixed with 1.3 parts of high activity proteolytic enzyme, and 0.3 part of detergent perfume was sprayed onto them. The final product has a zeolite content of 25%, an NTA content of 30%, sodium bentonite content of 5% and a water soluble sodium silicate solids content of 5%. The moisture content was 5% and the active deterative ingredient (polyethoxylated higher fatty alcohol) content was 20%. The bulk density was about 0.7 gr/cc. and the pH of its 1% solution was about 10.

- The detergent composition made by this method is a satisfactory heavy duty nonionic detergent but does deposit somewhat more zeolite-silicate aggregate on washed clothing that is line dried than does a corresponding composition made without any water soluble silicate solids.

Example 9C

- It is preferred that in such corresponding composition (Example 9B without silicate) there is also present about 0.1 to 0.5% of low molecular weight sodium polyacrylate, of the

- type previously described herein. Both the products of Example 9B and 9C wash laundry well and are especially effective in cold water washing, due at least in part to the bentonite contents thereof and the almost instantaneous dispersion that is observable when the detergent is added to wash water (which dispersion also diminishes time for any reaction between soluble silicate and zeolite to form objectionable aggregates).

Claims

1. Free flowing, spray dried beads, useful as a detergent or for the manufacture of a particulate built synthetic organic detergent composition, which detergents are of reduced particle deposition characteristics due to the presence of bentonite and a low content of water soluble silicate or absence of such silicate in the spray dried beads, comprising by weight from 5 to 60% of water softening aluminosilicate, 2 to 40% of bentonite, containing sufficient moisture to facilitate dispersion of the bentonite so as to inhibit deposition of aluminosilicate on the laundry being washed, 5 to 60% of water soluble builder or a mixture of such builders, 0 to 30% of water soluble synthetic organic detergent and 0 to 5% of water soluble silicate.
2. Beads as claimed in Claim 1, of a bulk density in the range of 0.2 to 0.9 gr/cc. and particle sizes in the range of No. 10 to 100, U.S. Sieve Series.
3. Beads as claimed in Claim 2 having a bulk density of 0.2 to 0.8 gr/cc.
4. Beads as claimed in anyone of the preceding claims in which the water softening aluminosilicate is a hydrated water softening zeolite containing from 15 to 25% by weight thereof of water of hydration.
5. Beads as claimed in anyone of the preceding claims in which the zeolite has an exchange capacity for calcium ions which is in the range 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite.
6. Beads as claimed in anyone of the preceding claims in which the zeolite is hydrated sodium zeolite.
7. Beads as claimed in anyone of the preceding claims in which the zeolite is Zeolite A.
8. Beads as claimed in anyone of the preceding claims in which the bentonite is a swelling clay.
9. Beads as claimed in anyone of the preceding claims in which the bentonite has a swelling capacity in water of 3 to 15 ml/gr.
10. Beads as claimed in anyone of the preceding claims in which the bentonite has a swelling capacity in the range of 7 to 15 ml/gr.
11. Beads as claimed in anyone of the preceding claims in which the bentonite exhibits a viscosity of 3 to 30 centipoises at 6% concentration in water.
12. Beads as claimed in anyone of the preceding claims in which the bentonite exhibits a viscosity in the range of 8 to 30 centipoises at 6% concentration in water.

13. Beads as claimed in anyone of the preceding claims in which the bentonite contains at least 2% of moisture on an anhydrous bentonite basis.

5 14. Beads as claimed in anyone of the preceding claims in which the bentonite includes at least 3% of moisture on an anhydrous bentonite basis.

10 15. Beads as claimed in anyone of the preceding claims in which the bentonite includes at least 4% of moisture.

16. Beads as claimed in anyone of the preceding claims in which the bentonite is beneficiated Wyoming bentonite.

15 17. Beads as claimed in anyone of the preceding claims in which the water soluble builder is polyphosphate, pyrophosphate, orthophosphate, borate, nitrilotriacetate, citrate, gluconate, carbonate or bicarbonate or a mixture
20 of two or more thereof.

18. Beads as claimed in anyone of the preceding claims in which the water soluble builder comprises carbonate, bicarbonate, polyphosphate or nitrilotriacetate, or mixture
25 thereof.

19. Beads as claimed in anyone of the preceding claims in which the water soluble builder comprises a nitrilotriacetate.

20. Beads as claimed in anyone of the preceding claims in which the water soluble builder comprises a polyphosphate.

21. Beads as claimed in anyone of the preceding claims in which the proportion of bentonite to zeolite is in the range of 1:4 to 1:1,
35 the proportion of water soluble builder to zeolite is within the range of 1:2 to 3:1 and the proportion of bentonite to water soluble builder is within the range of 1:10 to 1:1.

22. Beads as claimed in anyone of the preceding claims in which the proportion of bentonite:zeolite is in the range of 1:3 to 2:3, that
40 of water soluble builder:zeolite is within the range of 2:3 to 2:1 and that of bentonite:water soluble builder is within the range of 1:6 to 1:2.

23. Beads as claimed in anyone of the preceding claims comprising from 10 to 40% of water softening zeolite, 2 to 35% of bentonite, 10
45 to 50% of water soluble alkali metal builder salt or mixture thereof, 0 to 25% of water soluble synthetic anionic organic detergent and 0 to 3%
50 of water soluble silicate.

24. Beads as claimed in anyone of the preceding claims comprises from 15 to 35% of water softening zeolite, 5 to 20% of bentonite, 20
55 to 50% of water soluble alkali metal builder salt or mixture thereof, and 0 to 20% of water soluble synthetic anionic organic detergent and 0% of sodium silicate.

25. Beads as claimed in anyone of the preceding claims of a bulk density in the range of 0.2 to 0.9 gr/cc. and particle sizes in the range of
60 No. 10 to 100 U.S. Sieve Series, wherein the water softening aluminosilicate is hydrated water softening zeolite containing from 15 to 25% by
65 weight thereof of water of hydration and has an

exchange capacity for calcium ions which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, the bentonite is a swelling clay
70 having a swelling capacity, in water, of 3 to 15 ml/gr. and a viscosity of 3 to 30 centipoises at 6% concentration in water, and includes at least 2% of moisture on an anhydrous bentonite basis, a water soluble builder is present which is
75 polyphosphate, pyrophosphate, orthophosphate, borate, nitrilotriacetate, citrate, gluconate, carbonate or bicarbonate or a mixture of two or more thereof.

26. Beads as claimed in anyone of the preceding claims 1 to 24 comprising from 10 to 40% of hydrated sodium zeolite, 2 to 35% of bentonite, which bentonite is of a type which has
80 a swelling capacity in the range of 7 to 15 ml/gr. and is of a viscosity in the range of 8 to 30 centipoises of 6% concentration in water, 10 to 50% of water soluble alkali metal builder salt or mixture thereof, 0 to 25% of water soluble
85 synthetic anionic organic detergent and 0 to 3% of water soluble silicate.

27. Beads as claimed in anyone of the preceding claims 1 to 24 comprising from 15 to 35% of zeolite A, 5 to 20% of beneficiated Wyoming bentonite, 20 to 50% of water soluble
90 sodium builder salt or mixture thereof, 0 to 20% of water soluble synthetic anionic organic detergent and 0% of sodium silicate, and in which the proportion of bentonite:zeolite is in the range of 1:3 to 2:3, that of water soluble builder:zeolite
95 is within the range of 2:3 to 2:1 and that of bentonite:water soluble builder is within the range of 1:6 to 1:2.

28. Beads as claimed in anyone of the preceding claims 1 to 24 comprising from 15 to 40% of hydrated zeolite A containing 15 to 25%
105 by weight thereof of water of hydration and having an exchange capacity for calcium ions which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, 10 to 20% of bentonite which is a beneficiated Wyoming
110 bentonite of swelling capacity in the range of 7 to 15 ml/gr. and of a viscosity in the range of 3 to 30 centipoises at 6% concentration in water, and 20 to 60% of a nitrilotriacetate.

29. Beads as claimed in any of the preceding claims 1 to 24 comprising from 20 to 40% of hydrated zeolite A containing 15 to 25% by
115 weight thereof of water of hydration and having an exchange capacity for calcium ions which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, 10 to 20% of bentonite which
120 is a beneficiated Wyoming bentonite of swelling capacity in the range of 7 to 15 ml/gr. and of a viscosity in the range of 3 to 30 centipoises at 6% concentration in water, and 20 to 60% of sodium tri-polyphosphate.

30. Beads as claimed in anyone of the preceding claims containing a water soluble
130 silicate which is an alkali metal (M) silicate having

an $M_2O:SiO_2$ ratio in the range of 1:1.6 to 1:3.

31. Beads as claimed in any one of the preceding claims in which when water soluble synthetic detergent is not present the water soluble builder comprises polyphosphate, pyrophosphate orthophosphate, borate, nitrilotriacetate, gluconate or citrate or a mixture of two or more thereof.
32. Beads as claimed in claim 31 in which the water soluble builder comprises carbonate, bicarbonate, polyphosphate or nitrilotriacetate, or a mixture thereof, and the bentonite includes at least 3% of moisture on an anhydrous bentonite basis.
33. Beads as claimed in claim 32 in which the bentonite includes at least 4% of moisture, the water soluble builder comprises a nitrilotriacetate and no water soluble synthetic organic detergent nor any water soluble silicate is present.
34. Beads as claimed in Claim 32 in which the bentonite includes at least 4% of moisture, the water soluble builder comprises a polyphosphate and no water soluble synthetic organic detergent nor any water soluble silicate is present.
35. Beads as claimed in anyone of the preceding claims which comprise from 3 to 30% of water soluble synthetic organic detergent.
36. Beads as claimed in claim 35 which comprise from 5 to 30% of water soluble synthetic organic detergent.
37. Beads as claimed in claim 35 or claim 36 in which the water soluble synthetic organic detergent is an anionic detergent.
38. Beads as claimed in claim 37 in which the anionic detergent is a sodium linear alkylbenzene sulphonate wherein the alkyl group is of 10 to 18 carbon atoms, a sodium fatty alcohol sulphate wherein the alcohol is of 10 to 18 carbon atoms, or a sodium fatty alcohol ethoxylate sulphate wherein the fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 30 ethylene oxide groups per mol, or a mixture of two or more thereof.
39. Beads as claimed in anyone of claims 35 to 38 in which the proportion of anionic detergent in the beads is from 5 to 25%.
40. Beads as claimed in anyone of the preceding claims comprising from 15 to 40% of hydrated zeolite A containing 15 to 25% by weight thereof water of hydration and having an exchange capacity for calcium ions which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, 10 to 20% of bentonite which is a beneficiated Wyoming bentonite of swelling capacity in the range of 7 to 15 ml/gr. and of a viscosity in the range of 3 to 30 centipoises at 6% concentration in water, and 20 to 60% of NTA.
41. Beads as claimed in anyone of the preceding claims of a bulk density in the range of 0.2 to 0.8 gr/cc., wherein the aluminosilicate is hydrated zeolite A, the bentonite includes at least 3% moisture on an anhydrous bentonite basis, the water soluble builder, is a sodium salt of nitrilotri-

acetic acid (NTA), the water soluble silicate, if present, is sodium silicate of $Na_2O:SiO_2$ ratio in the range of 1:2 to 1:2.8, the moisture content of the beads is from 3 to 12% thereof, the proportion of bentonite:zeolite is in the range of 1:6 to 1:2, that of NTA:zeolite is in the range of 1:2 to 2:1, and that of bentonite:NTA is in the range of 1:6 to 1:2, and the percentages of hydrated zeolite, bentonite, NTA and silicate are respectively, within the ranges of 10 to 40%, 2 to 25%, 10 to 40%, and 0 to 5%.

42. Beads as claimed in anyone of the preceding claims of a bulk density in the range of 0.2 to 0.8 gr/cc., which comprises 5 to 30% of synthetic anionic organic detergent and in which the aluminosilicate is hydrated zeolite A, the bentonite includes at least 3% moisture on an anhydrous bentonite basis, the water soluble builder is a sodium salt of nitrilotriacetic acid (NTA) the synthetic anionic organic detergent is a sodium linear alkyl benzene sulphonate wherein the alkyl group is of 10 to 18 carbon atoms, a sodium fatty alcohol sulphate wherein the alcohol is of 10 to 18 carbon atoms, or a sodium fatty alcohol ethoxylate sulphate wherein the fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 30 ethylene oxide groups per mol, or a mixture comprising two or more thereof, the water soluble silicate, if present, is sodium silicate of $Na_2O:SiO_2$ ratio in the range of 1:2 to 1:2.8, the moisture content of the beads is from 3 to 12% thereof, the proportion of bentonite:zeolite is in the range of 1:6 to 1:1, that of NTA:zeolite is in the range of 1:3 to 3:1, that of bentonite:NTA is in the range of 1:10 to 1:1, and that of synthetic anionic organic detergent:zeolite is in the range of 1:1 to 1:4 and the percentages of hydrated zeolite, bentonite, NTA, synthetic anionic organic detergent, and silicate are respectively, within the ranges of 10 to 40%, 2 to 25%, 10 to 40%, 10 to 25% and 0 to 5%.
43. Beads as claimed in anyone of claims 1 to 39 comprising from 20 to 40% of hydrated zeolite A containing 15 to 25% by weight thereof of water of hydration and having an exchange capacity for calcium ions which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, 10 to 20% of bentonite which is a beneficiated Wyoming bentonite of swelling capacity in the range of 7 to 15 ml/gr and of a viscosity in the range of 3 to 30 centipoises at 6% concentration in water, and 20 to 60% of sodium tripolyphosphate.
44. Beads as claimed in anyone of claims 1 to 39 of a bulk density in the range of 0.2 to 0.8 gr/cc., wherein the aluminosilicate is hydrated zeolite A, the bentonite includes at least 3% moisture on an anhydrous bentonite basis, the water soluble builder is pentasodium tripolyphosphate or tetrasodium pyrophosphate or a mixture thereof, the water soluble silicate, if present, is sodium silicate of $Na_2O:SiO_2$ ratio in the range of 1:2 to 1:2.8, the moisture content of the beads is from 3 to 12% thereof, the proportion

of bentonite:zeolite is in the range of 1:6 to 1:2, that of total polyphosphate:zeolite is in the range of 1:2 to 2:1, and that of bentonite:total polyphosphate is in the range of 1:6 to 1:2, and the percentages of hydrated zeolite, bentonite, total polyphosphate, and silicate are respectively, within the ranges of 15 to 35%, 5 to 20%, 15 to 40% and 0 to 5%.

45. Beads as claimed in anyone of claims 1 to 39 of a bulk density in the range of 0.2 to 0.8 gr/cc. which comprise 5 to 30% of synthetic anionic organic detergent and in which the aluminosilicate is hydrated zeolite A, the bentonite includes at least 3% moisture on an anhydrous bentonite basis, the water soluble builder is pentasodium tripolyphosphate or tetrasodium pyrophosphate or a mixture thereof, the synthetic anionic organic detergent is a sodium linear alkyl benzene sulphonate wherein the alkyl group is of 10 to 18 carbon atoms, a sodium fatty alcohol sulphate wherein the alcohol is of 10 to 18 carbon atoms, or a sodium fatty alcohol ethoxylate sulphate wherein the fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 30 ethylene oxide groups per mol, or a mixture comprising two or more thereof, the water soluble silicate, if present, is sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:2 to 1:2.8, the moisture content of the beads is from 3 to 12% thereof, the proportion of bentonite:zeolite is in the range of 1:6 to 1:1, that of total polyphosphate:zeolite is in the range of 1:3 to 3:1, that of bentonite:total polyphosphate is in the range of 1:10 to 1:1, and that of synthetic anionic organic detergent:zeolite is in the range of 1:1 to 1:4 and the percentages of hydrated zeolite, bentonite, total polyphosphate, synthetic anionic organic detergent, and silicate are respectively, within the ranges of 10 to 40%, 2 to 25%, 10 to 50%, 10 to 25%, and 0 to 5%.

46. Beads as claimed in anyone of the preceding claims 1 to 34 in which no water soluble synthetic organic detergent is present.

47. Beads as claimed in anyone of the preceding claims 1 to 34 in which no water soluble silicate is present.

48. Beads as claimed in anyone of claims 1 to 34 which contain neither water soluble synthetic organic detergent nor water soluble silicate.

49. Beads as claimed in anyone of the preceding claims which comprise from 0.05 to 1% of polyacrylate of molecular weight in the

range of 1,000 to 5,000.

50. Beads as claimed in claim 1 substantially as specifically described herein with reference to anyone of Examples 1A, 2A to 2D, 3A to 3F, 4A to 4C, 5, 6A to 6, 7A to 7D or 9A.

51. A detergent composition which comprises beads as claimed in anyone of claims 1 to 50 having absorbed in them a nonionic detergent so that the percentage of such nonionic detergent in the composition is within the range of 8 to 30%.

52. A detergent composition as claimed in claim 51 in which the nonionic detergent is a condensation product of 6 to 22 mols of ethylene oxide and a higher fatty alcohol of 12 to 16 carbon atoms.

53. A detergent composition as claimed in claim 52 in which the nonionic detergent is a condensation product of 6 to 12 mols of ethylene oxide and a higher fatty alcohol of 12 to 16 carbon atoms.

54. A detergent composition as claimed in claim 52 or claim 53 in which the proportion of such nonionic detergent in the composition is within the range of 10 to 25%.

55. A detergent composition as claimed in claim 51 substantially as specifically described herein with reference to Example 1B, or Example 9B or Example 9C.

56. A detergent composition comprising a mixture of beads as claimed in anyone of claims 1 to 50 and particles of a composition as claimed in anyone of claims 51 to 55.

57. A detergent composition as claimed in claim 56 in which the particles have particle sizes in the range of No. 10 to 100, U.S. Sieve Series and are present in proportions, by weight, in the range of 1:10 to 10:1 and with the bulk densities of the beads before mixing thereof being within 0.1 gr/cc. of each other and of the bulk density of the final composition which is in the range of 0.2 to 0.9 gr/cc.

58. A detergent composition as claimed in claim 56 or claim 57 in which the beads are as claimed in claim 48 and the composition particles are as claimed in claim 51 when dependant on claim 48.

59. A detergent composition as claimed in claim 56 substantially as specifically described herein with reference to anyone of Examples 8A to 8C.